

Japanese Kokai Patent Application No. Hei 7[1995]-299468

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STERILIZING TREATMENT METHOD FOR WATER SYSTEM

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[There are no amendments to this patent.]

Abstract

Objective

The objective of this invention is to provide a sterilizing treatment method which has a significantly increased sterilizing power while an increase in the amount of the sterilizing agent is suppressed, and which has a high practical applicability for industrial water systems.

Constitution

A sterilizing treatment method for water systems characterized by the fact that it makes one or several types of organic bromine compounds, which are selected from the group of 1,4-dibromo-2,3-butanedione, brominated carboxylic acid derivatives, brominated alcohol derivatives, 3-bromopyruvic acid derivatives, N-bromosuccin imide, brominated hydantoin, and brominated isocyanuric acid, and a hydrogen peroxide-feeding compound react at the same time.

Claims

1. A sterilizing treatment method for a water system, characterized by the fact that it makes one or several types of organic bromine compounds, which are selected from the following listed group, and a hydrogen peroxide-feeding compound react at the same time:

1,4-dibromo-2,3-butanedione

brominated carboxylic acid derivatives represented by formula (I)

[Structure 1]



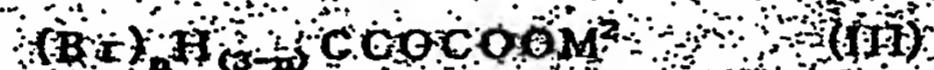
(Where R¹ represents a hydrogen atom or alkyl group having a carbon number of 6 or less; at least one of X¹ and X² represents a bromine atom, while the other represents a hydrogen atom or bromine atom; M¹ represents a hydrogen atom, alkali metal atom, alkaline-earth metal atom, alkyl having a carbon number of 6 or less, or hydroxyalkyl group, ammonium salt, or amine salt that has a total carbon number of 12 or less and may contain an oxygen atom and nitrogen atom.)

[Structure 2]



(Where R^2 represents a hydrogen atom or alkyl group having a carbon number of 6 or less; here, the alkyl group may have a bromine atom or hydroxyl group; at least one of X^3 and X^4 represents a bromine atom, and the other represents a hydrogen atom or bromine atom.)

3-bromopyruvic acid derivative represented by formula (III)

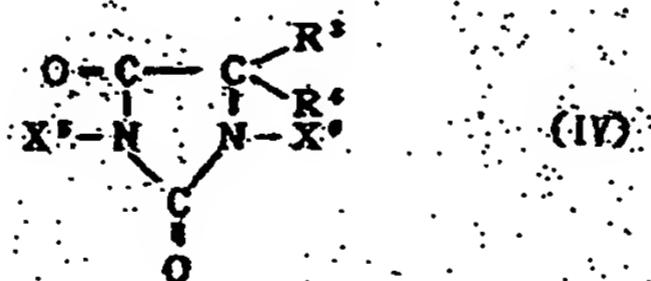


(Where n is 1 or 2; M^2 represents a hydrogen atom, alkali metal atom, alkaline-earth metal atom, alkyl group having a carbon number of 6 or less, or hydroxyalkyl group, ammonium salt, or amine salt that has a total carbon number of 12 or less and may contain an oxygen atom and nitrogen atom.)

N-bromosuccinimide

brominated hydantoin represented by formula (IV)

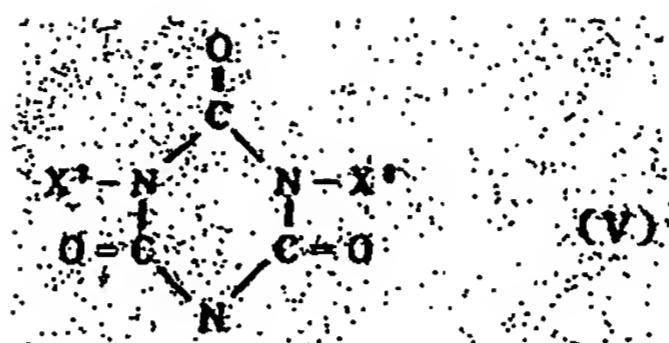
[Structure 3]



(Where at least one of X^5 and X^6 represents a bromine atom, and the other represents a bromine atom, chlorine atom, hydrogen atom, or alkali metal atom; R^3 and R^4 , which may be identical or different from each other, represent a hydrogen atom or C1-12 alkyl group.)

brominated isocyanuric acid represented by formula (V)

[Structure 4]



(Where at least one of X^7 , X^8 , and X^9 represents a bromine atom, and the others represent a hydrogen atom, bromine atom, chlorine atom, or alkali metal atom, and they may be identical or different from each other.)

2. The sterilizing treatment method for water system described in Claim 1, characterized by the fact that the hydrogen peroxide-feeding compound is hydrogen peroxide.
3. The sterilizing treatment method described in Claim 1 or 2, characterized by the fact that a solution of organic bromine compound is formed, and the hydrogen peroxide-feeding compound is premixed with the solution, followed by adding the mixture to the water system.

Detailed explanation of the invention

[0001]

Industrial application field

This invention pertains to a sterilizing treatment method for water systems. In particular, this invention pertains to a method for preventing problems of slime in cooling water systems, papermaking operations, etc.

[0002]

Prior art

Major applications of water in industry include cooling water, product treatment water, washing water, temperature adjusting water, etc. In these applications, problems caused by microbes take place frequently. In particular, when the sticky substance secreted by microbes is mixed with sand, iron rust, and organic substances in water, slime, which is a muddy substance, is formed, and slime causes many problems in operations in factories. For a cooling water system, in order to supplement water and reduce the cost of water, the water is often recycled. In such cases, because the cooling water is usually recooled in a cooling water column for use, the water is concentrated, and the concentrations of nutrients and contaminants increase at the same time, leading to active reproduction of microbes. In this case, as contaminants are adsorbed, formation of slime becomes even more significant. Due to attachment and reproduction of slime,

water passage through the strainer and heat transfer of the heat exchanger are impeded. Also, as the cross-sectional area of pipeline becomes smaller, the flow rate of the cooling water decreases, and in extreme cases, the pipeline may be clogged. Also, attachment of slime leads to pitting of the metal parts, etc. As measures against slime, people usually make use of various types of sterilizing agents, growth inhibiting agents and algicides to inhibit growth of microbes or kill them. In particular, chlorine-containing sterilizing agents are often used as they are inexpensive and can display effects on various species of microbes.

[0003]

Also, a large amount of industrial grade water is used in papermaking plants. However, it is hard to ensure a supply of high-quality industrial water. Also, there are problems in environmental protection and wastewater has to be discharged in a large amount. Consequently, efforts have been made to promote the recycling of water in the operations. However, when water is recycled, solutes in the recycled water as well as pulp, protein, talc, and other floating substances in it are concentrated. As a result, growth of microbes is promoted, and at the same time, the floating substances are deposited. Consequently, slime is formed not only in the water application system, but also in the white water pit, flowbox, pipeline, etc., in the papermaking process. Slime formed in the papermaking process grows to a certain degree and it is then separated from the wall and is mixed into pulp for papermaking. As a result, slime is contained in the paper product, leading to a significant decrease in the paper strength at the portion where the slime is contained. This causes paper breakage in the drying step of operation. Also, for the paper product containing slime, coloration, spots, dots, etc., are formed on the paper surface. This phenomenon is particularly significant for wood-free paper products, and leads to a significant decrease in the value of the product. As a result, formation of slime in the papermaking operation leads to significantly loss in economy. In the papermaking process, a large organic substance component is contained, and in this system, the effect of the chlorine-containing sterilizing agent decreases. Consequently, organic sterilizing agent is mainly used in this system, yet the effect is still insufficient.

[0004]

Organic bromine compounds are a type of organic sterilizing agent. Usually, an organic bromine compound is used alone. However, Japanese Kokai Patent Application No. Hei 5[1993]-170602 disclosed that when 2-bromo-2-nitro-1,3-propanediol is used together with a hydrogen peroxide-feeding compound, the effects can be augmented. In making the present invention, studies were made on the use of a hydrogen peroxide-feeding compound together with 2-bromo-4'-hydroxyacetophenone, 1-bromoacetoxy-2-propanol,

1-bromo-2-nitro-2-hydroxymethylpropanediol-1,3, 1,2-bis(bromoacetoxy)ethane, 1,4-bis(bromoacetoxy)-2-butene, and other organic bromine compounds. However, the excellent effect in inhibiting growth of microbes due to a synergic effect of said concurrent use of 2-bromo-2-nitro-1,3-propanediol and hydrogen peroxide-feeding compound was not observed at all.

[0005]

Problems to be solved by the invention

When the amount of sterilizing agent is increased, while the cost rises, an adverse influence on the equipment takes place, and this is undesired.

[0006]

The objective of this invention is to provide a sterilizing treatment method in industrial water systems, characterized by the fact that it can significantly increase the sterilizing power while lowering the amount of the sterilizing agent used.

[0007]

Another objective of this invention is to provide many types of compounds that can have a significantly increased sterilizing power when they are used together with a hydrogen peroxide-feeding compound. As a result, it is possible to expand the selection range of sterilizing agents to select an appropriate type of sterilizing agent corresponding to the specific situation.

[0008]

Means to solve the problems

In order to solve the aforementioned problems, the present inventors have performed extensive research on development of a sterilizing method that can display a high sterilizing effect while making use of a small amount of the sterilizing agent. As a result of this research, it was found that when a prescribed type of organic bromine compound and a hydrogen peroxide-feeding compound are used together, it is possible to display a high sterilizing power with a small amount of sterilizing agent. As a result, this invention was reached.

[0009]

That is, this invention provides a sterilizing treatment method for water systems characterized by the fact that it makes one or several types of organic bromine compounds, which are selected from the following listed group, and a hydrogen peroxide-feeding compound react at the same time:

1,4-dibromo-2,3-butanedione

brominated carboxylic acid derivatives represented by formula (I)

[0010]

[Structure 5]



(Where R^1 represents a hydrogen atom or alkyl group having a carbon number of 6 or less; at least one of X^1 and X^2 represents a bromine atom, while the other represents a hydrogen atom or bromine atom; M^1 represents a hydrogen atom, alkali metal atom, alkaline-earth metal atom, alkyl having a carbon number of 6 or less, or hydroxyl alkyl group, ammonium salt, or amine salt that has a total carbon number of 12 or less and may contain an oxygen atom and nitrogen atom.)
brominated alcohol derivative represented by formula (II)

[0011]

[Structure 6]



(Where R^2 represents a hydrogen atom or alkyl group having carbon number of 6 or less; here, the alkyl group may have a bromine atom or hydroxyl group; at least one of X^3 and X^4 represents a bromine atom, and the other represents a hydrogen atom or bromine atom.)
3-bromopyruvic acid derivative represented by formula (III)

[0012]



(Where n is 1 or 2; M^2 represents a hydrogen atom, alkali metal atom, alkaline-earth metal atom, alkyl group having a carbon number of 6 or less, or a hydroxyalkyl group, ammonium salt, or

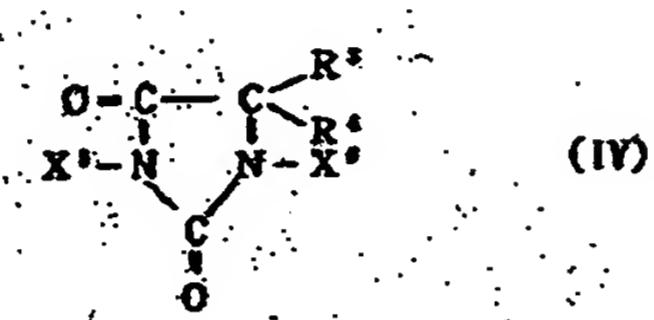
amine salt that has a total carbon number of 12 or less and may contain an oxygen atom and nitrogen atom.)

N-bromosuccinimide

brominated hydantoin represented by formula (IV)

[0013]

[Structure 7]

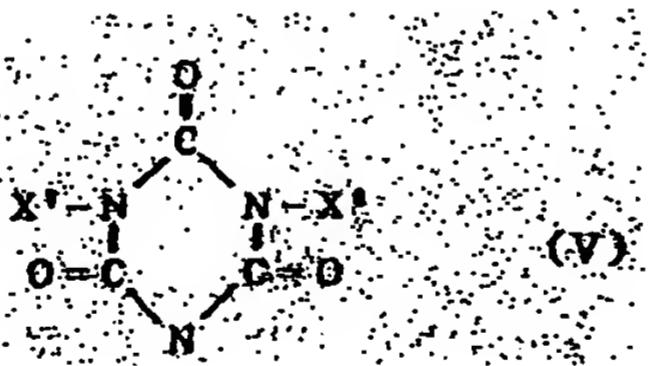


(Where at least one of X^5 and X^6 represents a bromine atom, and the other represents a bromine atom, chlorine atom, hydrogen atom, or alkali metal atom; R^3 and R^4 , which may be identical or different from each other, represent a hydrogen atom or C1-12 alkyl group.)

brominated isocyanuric acid represented by formula (V)

[0014]

[Structure 8]



(Where at least one of X^7 , X^8 , and X^9 represents a bromine atom, and the others represent a hydrogen atom, bromine atom, chlorine atom, or alkali metal atom, and they may be identical or different from each other.)

[0015]

For the brominated carboxylic acid derivatives represented by formula (I), R^1 represents a hydrogen atom or alkyl group having a carbon number of 6 or less. Here, the alkyl group may be a straight chain or branched chain, and the carbon number of the alkyl group is preferably in the range of 1-4. Examples of the alkyl groups include methyl, ethyl, n-propyl, isopropyl, n-butyl,

n-hexyl, etc. One of X^1 and X^2 is a bromine atom, while the other is a hydrogen atom or bromine atom. M^1 represents a hydrogen atom, alkali metal atom, alkaline-earth metal atom, alkyl with carbon number of 6 or less, or a hydroxyalkyl group, ammonium salt, or amine salt that has a total carbon number of 12 or less and may contain an oxygen atom and nitrogen atom. Examples of alkali metal atoms include sodium, potassium, etc. Examples of alkaline-earth metal atoms include calcium, barium, etc. The alkyl or hydroxyalkyl group has a carbon number of 6 or less, preferably 3 or less, and it may have a straight-chain or branched-chain structure. Examples include methyl, ethyl, n-propyl, isopropyl, n-butyl, n-hexyl, 2-ethylhexyl, hydroxyethyl, 2-hydroxypropyl, etc. The amines have a total carbon number of 12 or less, preferably 8 or less, and may contain an oxygen atom and nitrogen atom. The amines may have any of straight-chain, branched-chain, or cyclic structure. They may be any of primary amines, secondary amines, and tertiary amines. Examples of the amines include methylamine, propylamine, hexylamine, cyclohexylamine, diethylamine, triethylamine, monoethanolamine, morpholine, piperazine, etc.

[0016]

Examples of brominated carboxylic acid derivatives represented by formula (I) as explained above include bromoacetic acid, 2-bromopropionic acid, 2-bromo-n-butyric acid, 2-bromohexanoic acid, methyl ester of bromoacetic acid, tetraethylammonium salt of bromoacetic acid, propylamine salt of 2-bromopropionic acid, etc.

[0017]

For brominated alcohol derivatives represented by formula (II), R^2 represents a hydrogen atom or alkyl group having carbon number of 6 or less. Here, the alkyl group may contain a bromine atom and hydroxyl group, and it may be a straight chain or branched chain, and the carbon number of the alkyl group is preferably in the range of 1-4. Examples of alkyl groups include methyl, ethyl, n-propyl, isopropyl, n-butyl, n-hexyl, etc. At least one of X^3 and X^4 is a bromine atom, while the other is a hydrogen atom or bromine atom. Examples of brominated alcohol derivatives represented by formula (II) include 2-bromoethanol, 2,3-dibromopropanol, 2,2-dibromopentyl glycol, 2,3-dibromo-1-propanol, etc.

[0018]

For the 3-bromopyruvic acid derivatives represented by formula (III), n is 1 or 2. M^2 represents a hydrogen atom, alkali metal atom, alkaline-earth metal atom, alkyl having a carbon number of 6 or less, or a hydroxyalkyl group, ammonium salt, or amine salt that has a total carbon number of 12 or less and may contain an oxygen atom and nitrogen atom. Examples of alkali metal atoms include sodium, potassium, etc. Examples of alkaline-earth metal atoms

include calcium, barium, etc. The alkyl or hydroxyalkyl group has a carbon number of 6 or less, or preferably 3 or less, and it may have a straight-chain or branched-chain structure. Examples include methyl, ethyl, n-propyl, isopropyl, n-butyl, n-hexyl, 2-ethylhexyl, hydroxyethyl, 2-hydroxypropyl, etc. The amines have a total carbon number of 12 or less, or preferably 8 or less, and may contain an oxygen atom and nitrogen atom. The amines may have any of straight-chain, branched-chain, or cyclic structure. They may be any of primary amines, secondary amines, and tertiary amines. Examples of the amines include methylamine, propylamine, hexylamine, cyclohexylamine, diethylamine, triethylamine, monoethanolamine, morpholine, piperazine, etc. Examples of the brominated 3-bromopyruvic acid derivatives represented by formula (III) include 3-bromopyruvic acid, as well as its methyl ester, ethyl ester, ethylamine salt, morpholine salt, etc.

[0019]

For the brominated hydantoin represented by formula (IV), examples of the alkali metal atoms in X^5 and X^6 include sodium, potassium, etc. When R^3 and R^4 represent an alkyl group, its carbon number is preferably in the range of 1-3. Examples of the alkyl groups include methyl, ethyl, n-propyl, and isopropyl. Examples include 1-bromo-3-chloro-5,5-dimethylhydantoin, 1,3-dibromo-5,5-dimethylhydantoin, etc.

[0020]

For brominated isocyanuric acid represented by formula (V), examples of the alkali metal atoms in X^7 , X^8 , and X^9 include sodium, potassium, etc. Examples of brominated isocyanuric acid represented by formula (V) include 1,3,5-tribromoisocyanuric acid, 1,3-dibromo-5-chloroisocyanuric acid, etc. According to this invention, these organic bromine compounds may be used either alone or as a mixture of several types.

[0021]

According to this invention, the hydrogen peroxide-feeding compound refers to a compound that can generate hydrogen peroxide in water. Examples of such compounds include hydrogen peroxide, sodium percarbonate, potassium percarbonate, and other percarbonate salts, peracetic acid, and other organic peroxy acid salts, etc. Among them, hydrogen peroxide is preferred as it can be handled easily, has a low cost, and has other advantages. According to this invention, the hydrogen peroxide-feeding compounds may be used either alone or as a mixture of several types.

[0022]

In the sterilizing treatment method of this invention, it is required that the aforementioned organic bromine compound and hydrogen peroxide-feeding compound act at the same time in the water system. It is preferred that the organic bromine compound be prepared as a solution with an appropriate concentration, and it be mixed with an aqueous solution of the hydrogen peroxide-feeding compound prepared separately, followed by adding the mixture into the water system. When the organic bromine compound and hydrogen peroxide-feeding compound are mixed, one may simply add the hydrogen peroxide-feeding compound into the solution of the organic bromine compound. Also, in some cases, it is preferred that the solution of the organic bromine compound be made acidic, and the hydrogen peroxide-feeding compound be added into said solution. Also, when the organic bromine compound is to be prepared as a solution yet is difficult to dissolve, one may dissolve it in ethylene glycol, polyethylene glycol monoethyl ether, or the like, and as needed, add a surfactant for emulsification or dispersion. This is an effective method. There is no special limitation on the mixing method in this invention.

[0023]

According to this invention, the organic bromine compound and hydrogen peroxide-feeding compound have their intrinsic sterilizing effects, respectively. However, when said organic bromine compound and hydrogen peroxide-feeding compound are mixed, the mixture displays a high penetrating ability, so that a significantly high sterilizing function is displayed. This is a new finding not found in the conventional knowledge. Consequently, one may select the mixing ratio of organic bromine compound and hydrogen peroxide-feeding compound at will within the range where said function can be displayed. In order to display a significant effect for the method of this invention, it is necessary to have a sufficient amount of hydrogen peroxide-feeding compound for activating bromine atoms in an organic bromine compound. That is, the amount of hydrogen peroxide-feeding compound added should be sufficient to activate the bromine atoms in the organic bromine compound. The ratio of hydrogen peroxide-feeding compound to organic bromine compound which ensures a display of synergic effect is in the range of 1-100 fold (molar ratio), or preferably in the range of 2-10 fold (molar ratio). If this range is not observed, although the effect is realized, the effect nevertheless will level off with respect to a further increase in the amount, and this is undesired.

[0024]

The amount added into the water system depends on the count of microbes in the water, water quality, temperature, and other operation conditions. Usually, with respect to the amount of water kept in the system, the concentration of organic bromine compound should be in the

range of 0.01-1000 ppm, preferably in the range of 0.1-100 ppm, more preferably in the range of 1-10 ppm. If the concentration of the organic bromine compound is less than 0.01 ppm, the effect becomes insignificant. On the other hand, if the concentration is over 1000 ppm, although the effect is displayed, the effect nevertheless levels off with respect to an increase in the amount added, and this is undesired from the economical viewpoint.

[0025]

For the method of this invention, it is possible to add other slime-inhibiting agents, sterilizing agents, slime-dispersing agents, corrosion-inhibiting agents, scale-inhibiting agents, etc., at the same time. There is no special limitation on them. Also, there is no special limitation on the addition of sodium bromide (NaBr) to other inorganic bromine compounds, sodium hypochlorite or other chlorine-containing agents used together with the sterilizing agent of this invention.

[0026]

Operation

For the conventional sterilizing agent, the only purpose is to kill microbes. The sterilizing agent is added so as to have microbes dispersed in the sterilizing water or the like. As an index of the effect of killing microbes, the change in turbidity and the index using the colony counting method have been developed. However, in a practical system, the sticky substance secreted by microbes is mixed with sand, iron rust, and organic substances in water, so that slime, a muddy substance, is formed, in which the microbes live. Consequently, even when the agent has an ability to kill the microbes floating in the water, the sterilizing effect on microbes covered with such organic substances becomes insufficient. As a matter of fact, it has been reported that microbes attached to [slime] have a higher resistance against chemical agents than that of the floating microbes (see: *Biseibutsu no seitai* [Living state of microbes] 16 (published by Gakkai Publication Center), p. 37). In order to prevent slime, several methods have been developed, such as the method described in Japanese Kokai Patent Application No. Hei 3[1991]-193, in which glucanase is used to decompose the polysaccharides secreted by the microbes, and the method described in Japanese Kokai Patent Application No. Hei 5[1993]-155719, which points out the necessity to lower the viscosity of the polysaccharides secreted by the microbes when slime is to be peeled off. It has been found that, in addition to the microbes themselves, it is necessary to take into consideration the entire system of the slime, including the peripheral organic substances. Also, microbes are covered with many types of extracellular polysaccharides, capsular polysaccharides, etc., secreted by the microbes themselves. In many cases, the sterilizing agent is simply unable to reach the body of the microbe. Such microbes that can

secrete polysaccharides can also form slime easily. If no effect can be displayed on the microbes with a high ability to form slime, the sterilizing agent would be useless. As the conventional sterilizing agents were developed without considering this problem, although addition of the conventional sterilizing agents does lead to a decrease in the microbe count in water, problems of slime still occur in many cases. This is a contradiction. This invention was reached as the present inventors realized this problem.

[0027]

It has been known that the sterilizing function of bromine compounds is due to formation of hypobromous acid from sodium bromide and sodium hypochlorite. Due to this effect, the sterilizing effect at high pH is better than that when sodium hypochlorite is used alone (J.E. Alleman etc., Water Reuse Symposium 5 of American Water Works Association Aug, 1987, J.E. Alleman etc., 42nd Annual Purodue Industrial Water Conference May, 1987). Also, it is well known that brominated acetic acid has an effect in preventing or treating Boraginaceae (Japanese Kokoku Patent No. Sho 52[1977]-84), alkyl ester of brominated acetic acid has an effect in suppressing reproduction of algae (Japanese Kokoku Patent No. Sho 60[1985]-46082), brominated nitroalkyl alcohol has sterilizing power by itself (Japanese Kokai Patent Application No. Sho 59[1984]-175406), etc. On the other hand, for combinations formed with hydrogen peroxide, a synergic effect has been obtained for the combination with 2-bromo-2-nitro-1,3-butanediol. However, no synergic effect has been observed with other nitro alcohols and bromoacetoxy compounds (Japanese Kokai Patent Application No. Hei 5[1993]-170602). However, in the aforementioned methods, also, the effect in sterilizing microbes covered with slime or polysaccharides is insufficient.

[0028]

This invention provides a slime-inhibiting method for industrial water systems characterized by the fact that not only can it kill microbes floating in water, but can also kill microbes living in slime; besides, it can also act directly on microbes soaked and covered with extracellular polysaccharides and capsular polysaccharides so as to kill them.

[0029]

Application examples

In the following, this invention will be explained in detail with reference to application examples. However, this invention is not limited to these application examples.

[0030]

Organic bromine compounds used in application examples

Compound A: 1,4-dibromo-2,3-butanedione (reagent, product of Wako Pure Chemical Industries, Ltd.)

Compound B: bromoacetic acid (reagent, product of Kanto Chemical Co., Ltd.)

Compound C: 2-bromopropionic acid (reagent, product of Kanto Chemical Co., Ltd.)

Compound D: 2-bromo-n-butyric acid (reagent, product of Kanto Chemical Co., Ltd.)

Compound E: 2-bromoethanol (reagent, product of Kanto Chemical Co., Ltd.)

Compound F: 2,3-dibromopropanol (reagent, product of Wako Pure Chemical Industries, Ltd.)

Compound G: 3-bromopyruvic acid ethyl ester (reagent, product of Aldrich Co.)

Compound H: N-bromosuccinimide (reagent, product of Kanto Chemical Co., Ltd.)

Compound I: 1,3-dibromo-5,5-dimethylhydantoin (product of Teijin, Ltd.)

Compound J: 1,3,5-tribromoisocyanuric acid

[0031]

Compound J was prepared as follows. 10 g bromine were added to 60 mL of ion-exchanged water, and the mixture was agitated under ice cooling. While being agitated, a solution prepared by dissolving 2 g cyanuric acid and 3 g potassium hydroxide was slowly added dropwise. During this period, the temperature was kept at 0-3°C. After the end of the dropwise addition, the mixture was further agitated for 30 min. Then, the deposited crystal was filtered and was well washed with cooled fresh water to form 1,3,5-tribromoisocyanuric acid.

[0032]

Said organic bromine compound was dissolved in a mixed solution of acetone-water (1:1 ratio by volume) and the obtained solution was used in the test.

[0033]

Organic bromine compounds used in application examples

0.2 mL hydrogen peroxide (30%) was added to 1 mL of 1 wt% of the organic bromine compound to form a sample for tests. Also, as a control, 0.2 mL of an aqueous solution of hydrogen peroxide (30%) was added to 1 mL of pure water. Also, as another control, 0.2 mL of pure water was added to 1 mL of a 1 wt% solution of the organic bromine compound.

[0034]

Strains of bacteria used in the application examples

Escherichia coli (IAM-12119)

Staphylococcus aureus (IAM-12544)

Pseudomonas aeruginosa (IFO-12689)

Pseudomonas fluorescens (IAM-1154)

Bacillus coagulans (IFO-12583)

Beijerinckia indica (IFO-3745)

Alcaligenes latus B-16 (FERM BP-2015)

Xanthomonas campestris (IFO-13551)

Trichoderma viride (IFO-5720)

Saccharomyces cerevisiae (IAM-4274)

[0035]

Application Example 1

In 10 mL of sterilized water, each of the following bacteria, adjusted to a logarithmic regeneration period (1 platinum loop for each of them), was added to form a suspension:

Escherichia coli, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Pseudomonas fluorescens*, and *Bacillus coagulans*. After 0.1 mL of the bacterial solution was dripped on a plate of nutrient broth (pH = 6.8) (product of Diffico Co.), it was uniformly spread with a Conradi's rod. At the central portion of the spread, a 5-mm-diameter sterilized glass filter was arranged, and 0.02 mL of an organic bromine composition sample was dripped.

[0036]

After culturing at 30°C for 3 days, the area where growth of bacteria was inhibited was measured. For the portion where the organic bromine compound soaks, there was no growth of bacteria. Consequently, the growth inhibiting area of bacteria becomes larger where the organic bromine compound has a higher soaking ability in an agar culture medium (in organic substances), and a higher sterilizing power is displayed. The results are listed in Table 1.

[0037]

Table 1. Area where growth is inhibited by organic bromine compounds

	Application Example					Comparative Example				
	Organic bromine compound - aqueous hydrogen peroxide solution					Organic bromine compound alone, or aqueous hydrogen peroxide solution alone				
	<i>Escherichia coli</i>	<i>Staphylococcus aureus</i>	<i>Pseudomonas aeruginosa</i>	<i>Pseudomonas fluorescens</i>	<i>Bacillus coagulans</i>	<i>Escherichia coli</i>	<i>Staphylococcus aureus</i>	<i>Pseudomonas aeruginosa</i>	<i>Pseudomonas fluorescens</i>	<i>Bacillus coagulans</i>
Not added						0.2	0.2	0.2	0.2	0.2
HIO_2 (alone)						0.2	0.2	0.2	0.2	0.2
Compound-A	32	27	29	23	25	1.6	2.0	1.8	0.5	0.4
Compound-B	34	31	33	27	28	0.2	0.2	0.2	0.2	0.2
Compound-C	32	31	30	34	33	0.2	0.2	0.2	0.2	0.2
Compound-D	29	26	26	27	28	0.2	0.2	0.2	0.2	0.2
Compound-E	36	31	29	18	21	0.2	0.2	0.2	0.2	0.2
Compound-F	42	32	39	37	33	0.5	0.3	0.8	0.2	0.2
Compound-G	21	22	23	25	17	0.4	0.2	0.2	0.2	0.2
Compound-H	28	27	25	20	19	3.6	2.8	1.8	0.7	0.9
Compound-I	54	48	47	42	43	15	15	12	10	11
Compound-J	59	57	49	47	45	16	18	14	11	9

[0038]

As can be seen from these results, compared with the case when organic bromine compound or aqueous hydrogen peroxide solution is used alone, when a combination of the organic bromine compound and aqueous hydrogen peroxide solution is used, the penetrating power is improved significantly, and it can kill microbes in a wide range.

[0039]

Application Example 2

In 10 mL of sterilized water, each of the following bacteria, adjusted to a logarithmic regeneration period (1 platinum loop for each of them), was added to form a suspension: *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Pseudomonas fluorescens*, and *Bacillus coagulans*. After 0.1 mL of the bacterial solution was dripped on a plate of nutrient broth, and glycine Na buffer was added to adjust the pH to 8.5, it was uniformly spread with a Conradi's rod. At the central portion of the spread, a sterilized glass filter was arranged, and 0.02 mL of organic bromine composition solution was dripped on it in the same way as Application Example 1. After culturing at 30°C for 3 days, the area where growth of bacteria was inhibited was measured. The results are listed in Table 2.

[0040]

Table 2. Area where growth is inhibited by organic bromine compound

	Application Example					Comparative Example				
	Organic bromine compound - aqueous hydrogen peroxide solution					Organic bromine compound alone, or hydrogen peroxide solution alone				
	<i>Escherichia coli</i>	<i>Staphylococcus aureus</i>	<i>Pseudomonas aeruginosa</i>	<i>Pseudomonas fluorescens</i>	<i>Bacillus coagulans</i>	<i>Escherichia coli</i>	<i>Staphylococcus aureus</i>	<i>Pseudomonas aeruginosa</i>	<i>Pseudomonas fluorescens</i>	<i>Bacillus coagulans</i>
Not added						0.2	0.2	0.2	0.2	0.2
HIO ₂ (alone)						0.2	0.2	0.2	0.2	0.2
Compound-A	7.8	7.5	7.2	6.3	6.4	0.8	0.5	0.4	0.3	0.8
Compound-B	7.2	7.1	7.0	7.0	6.9	0.2	0.2	0.2	0.2	0.2
Compound-C	6.9	5.4	5.3	4.7	5.3	0.2	0.2	0.2	0.2	0.2
Compound-D	6.7	7.2	6.5	3.8	6.4	0.2	0.2	0.2	0.2	0.2
Compound-E	5.6	5.1	5.1	4.8	4.8	0.2	0.2	0.2	0.2	0.2
Compound-F	4.9	4.9	4.9	3.0	4.7	0.2	0.2	0.2	0.2	0.2
Compound-G	4.4	3.8	3.9	3.1	3.3	0.2	0.2	0.2	0.2	0.2
Compound-H	4.6	5.3	5.3	3.2	3.6	2.0	1.4	0.8	0.4	0.7
Compound-I	18	16	16	11	11	9.8	8.7	6.5	2.1	1.9
Compound-J	15	16	14	14	13	8.3	8.1	7.9	4.6	4.3

[0041]

As can be seen from these results, even when pH = 8.5, a combination of organic bromine compound and aqueous hydrogen peroxide solution has excellent penetrating power, and it can kill microbes in a wide range.

[0042]

Application Example 3

Trichoderma viride (fungi) cultured on PDA plate (product of Tanabe Pharmaceutical Co., Ltd.) was added to sterilized water to form a spore suspension with a microbe count of 1×10^8 cells/mL. Also, 1 platinum loop of *Saccharomyces cerevisiae* (yeast) that had been adjusted to a logarithmic regeneration period was added to 10 mL of sterilized water to form a suspension. For each of said microbe solutions, the solution was dripped on a PDA plate, and it was then uniformly spread with a Conradi's rod. At the central portion of the spread, a sterilized glass filter was arranged, and 0.02 mL of organic bromine composition solution was dripped. After culturing at 25°C for 5 days, the area where growth of bacteria was inhibited was measured. The results are listed in Table 3.

[0043]

Table 3. Area where growth is inhibited by organic bromine compound

	<i>Trichoderma viride</i>		<i>Saccharomyces cerevisiae</i>	
	Application Example	Comparative Example	Application Example	Comparative Example
Not added		0.2		0.2
Hydrogen peroxide used alone		0.2		0.2
	Organic bromine compound + hydrogen peroxide	Organic bromine compound used alone	Organic bromine compound + hydrogen peroxide	Organic bromine compound used alone
Compound-A	38	1.8	16	0.6
Compound-B	35	0.2	14	0.2
Compound-C	34	0.2	17	0.2
Compound-D	30	5.5	13	0.7
Compound-E	43	24	29	21
Compound-F	41	19	26	15

[0044]

As can be seen from these results, when a combination of organic bromine compound and aqueous hydrogen peroxide solution is used, penetrating power is high, and it also displays a high sterilizing power for fungi and yeast.

[0045]

Application Example 4

Sterilizing tests in water were performed for each of the following listed strains of bacteria with bodies covered with polysaccharides: *Beijerinckia indica*, *Alcaligenes latus* B-16, and *Xanthomonas campestris*. As a control, *Escherichia coli* was used. For each of these species, 1 platinum loop of bacteria was added to 100 mL sterilized water to form a suspension. After the bacteria count was measured for the microbe suspension using the plate counting method, 1 mL of the solution of organic bromine compound was added, and the mixture was shaken at 30°C for 1 h. Then, the bacteria count was measured again. From the values of bacteria count measured before and after addition of the organic bromine compound composition, the survival rate (%) was determined for evaluating the organic bromine compound composition. The results are listed in Table 4.

[0046]

Table 4. Results of sterilizing tests of various organic bromine compounds

(Survival rate %)

Species of bacteria	<i>Beijierinchia indica</i>		<i>Alcaligenes latus</i> B-16		<i>Xanthomonas campestris</i>		<i>Escherichia coli</i>	
Initial bacterial count	6×10^7		4×10^7		7×10^7		1×10^8	
	Application Example	Comparative Example						
Hydrogen peroxide alone		100		100		100		1×10^{-2}
	Organic bromine compound + hydrogen period	Organic bromine compound alone	Organic bromine compound + hydrogen period	Organic bromine compound alone	Organic bromine compound + hydrogen period	Organic bromine compound alone	Organic bromine compound + hydrogen period	Organic bromine compound alone
Compound-A	4×10	100	2×10	100	8×10	100	6×10	100
Compound-B	5×10	100	3×10	100	1×10	100	7×10	100
Compound-C	1×10	100	6×10	100	9×10	100	9×10	100
Compound-E	2×10	100	8×10	100	1×10	100	5×10	100
Compound-H	1×10	100	5×10	100	8×10	100	2×10	100
Compound-I	≈ 0	90	≈ 0	90	≈ 0	50	≈ 0	1×10^{-3}
Compound-J	≈ 0	95	≈ 0	90	≈ 0	70	≈ 0	1×10^{-3}

[0047]

As can be seen from these results, when an aqueous hydrogen peroxide solution is used alone, although *Escherichia coli* that is used as a control displays a significant sterilizing effect, its sterilizing effect on the bacterial strains *Beijierinchia indica*, *Alcaligenes latus* B-16, and *Xanthomonas campestris* with bodies covered with polysaccharides is not displayed. This indicates that these bacteria are protected by polysaccharides. Also, when an organic bromine compound alone is used, no sterilizing effect is displayed on any species of bacteria. On the other hand, when the organic bromine compound and aqueous hydrogen peroxide solution are combined according to this invention, a high sterilizing effect is displayed not only on *Escherichia coli*, but also on bacteria strains *Beijierinchia indica*, *Alcaligenes latus* B-16, and *Xanthomonas campestris* with bodies covered with polysaccharides.

[0048]

Effect of the invention

According to the method of this invention, [the sterilizing treatment agent] not only can kill microbes in water, but also displays a high penetrating power through the slime formed from the sticky substance secreted by microbes mixed with sand, iron rust, and organic substances in water, so that it can kill microbes living inside the slime, and it can penetrate through

extracellular polysaccharides and capsular polysaccharides to act directly and kill microbes covered with them. As a result, the slime-inhibiting efficiency is very high. Also, as it acts inside the slime, the slime that has been formed loses its coagulating property, so that the slime is dispersed and removed. In addition, compared with the conventional chlorine-containing sterilizing agents, the method of this invention displays a higher sterilizing power even at a high pH level, and it has less corrosion. Consequently, it can be used preferably in industry.

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